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GB 1406082

GB 1212873

GB 1172466

GB 0727748

EP A1 0230391

US 4483749

US 3546088

US 2603593

Note: GB 1212873 and US 3546088 are equivalent;

GB 0727748 and US 2603593 are equivalent;

(58) Field of search

C7B

Selected US specifications from IPC sub-class

C25D

(54) Electrolytic treatment device

(57) A device for electrolytically treating, e.g. polishing, a metal surface 11 comprises a housing 1 for making sealing contact with the surface 11 thereby to enclose an area for electropolishing, and an electrolyte chamber 5 defined within the housing 1 bounded in part by the area when the housing is connected to the surface. A cathode 4 for contacting the electrolyte during use is also mounted within the housing 1. The sealing contact may be made by means of a deformable seal 12, 13. In operation, electrolyte is provided in the chamber 1 in contact with the surface 11 and the cathode 4 and an electric current is passed through the electrolytic cell constituted by the surface 11 (as anode), the electrolyte and the cathode 4 in order to treat the surface by anodic oxidation. Preferably, the electrolyte passes through the chamber 5.

The seals 12, 13 may comprise a tube of hard elastomer filled with a softer silicone rubber.

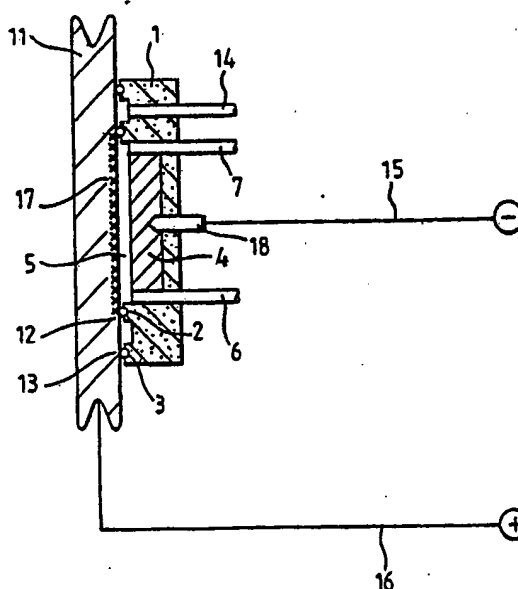


Fig. 4.

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Fig. 1.

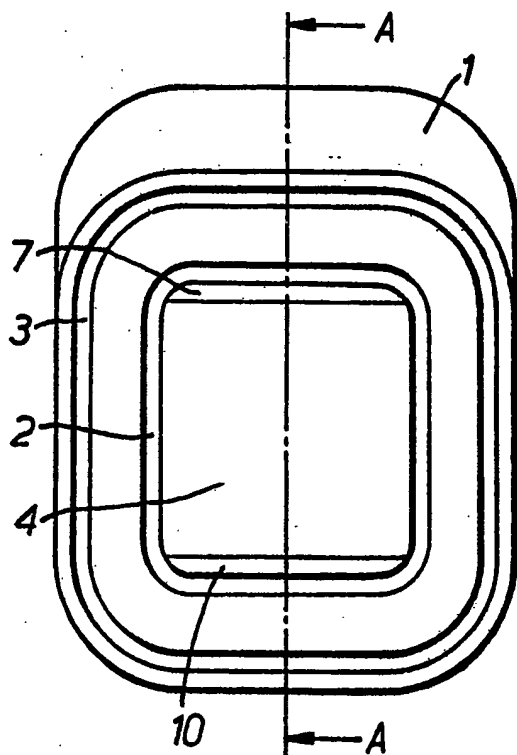


Fig. 2.

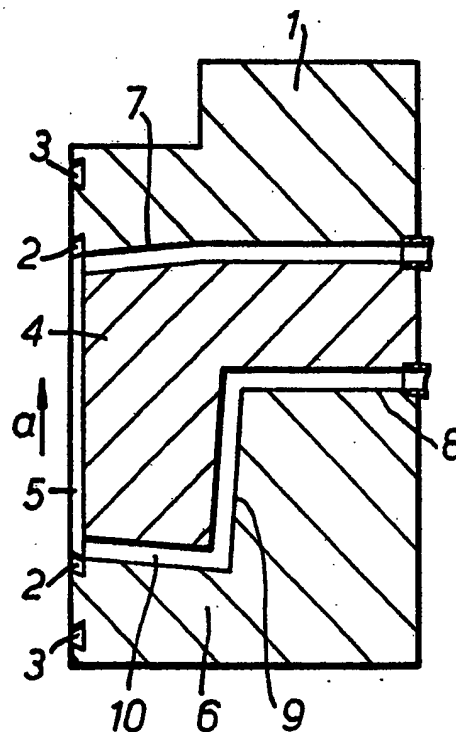
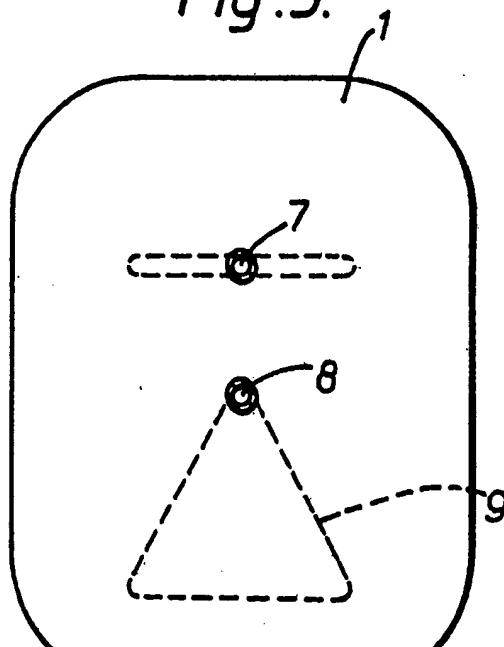


Fig. 3.



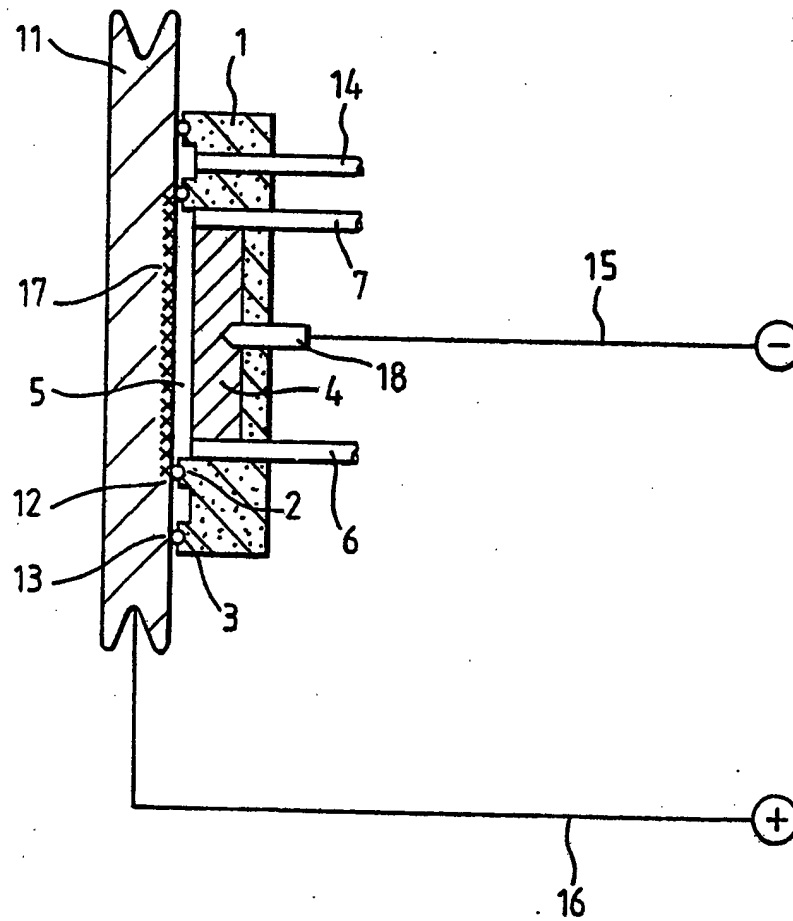


Fig.4.

Electrolytic Treatment Device

This invention relates to a device for electrolytically treating a metal surface.

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Electrolytic treatment to modify surfaces is a known process involving establishing an electrolytic cell where an object having a surface to be treated constitutes an electrode thereof, and passing an electric current through the cell under conditions such that the surface is modified by removal of material therefrom, e.g. to improve its appearance and/or structure. Electrolytic polishing (also known as electropolishing) is a form of such treatment and is described in GB-A-530,041, for example. The patent describes the process of electrolytically polishing objects of Fe, Co, Ni, Cr, and their alloys, comprising the step of making the object the anode in an acid aqueous electrolytic bath containing ions having a position in the lyotropic series according to Cooper following after the sulphate ion and capable of forming easily soluble salts with said metals, using a current density sufficient to cause a removal from the surface of the object of solid anodic oxidation products primarily formed in the treatment. An example of an acid aqueous electrolytic bath described in the above-mentioned patent is a nitric acid bath.

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This invention includes a device for electrolytically treating a metal surface comprising

a housing connectable to the surface, in liquid-tight sealing contact therewith, to enclose an area of the surface for electrolytic treatment;

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an electrolyte chamber defined within the housing and, when the housing is connected to the surface, bounded in

part by said area of the surface;

5 a cathode mounted within the housing for contacting electrolyte in the electrolyte chamber thereby to establish an electrolytic cell comprising the cathode, the electrolyte and the surface as anode; and

means for connecting the cathode and the surface, as anode, to a source of electromotive force.

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Conveniently, the electrolyte chamber has an inlet for supplying electrolyte to the chamber and an outlet for removing used electrolyte from the chamber. Preferably, the electrolyte chamber is bounded in part by the cathode also.

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In operation of the device, it is connected to the surface to be treated, electrolyte is provided in the electrolyte chamber, the cathode and the surface are connected to a source of electromotive force, and an electric current is passed. The electrolytic cell comprising the electrolyte, the cathode and the surface (as anode) is thereby operated and material removed electrolytically from the surface. The electrolyte may be static, for example when the device is small (e.g. the treatment area is 2 cm²) and a low current is to be applied for a short time, or it may be flowing, for example when the device is larger and there is a need to dissipate heat generated by the electric current.

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The housing has to be connectable in liquid-tight sealing contact with the surface in order to define an area thereof for treatment and to prevent electrolyte from flowing onto parts of the surface other than the area being treated. The housing may therefore be provided with one or more continuous deformable seals for making contact with

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the surface. Such seals are particularly useful for connecting the housing to an uneven surface. It is particularly preferred that there is a plurality of concentric deformable seals, means being provided for
5 generating a vacuum therebetween to cause the seals to engage the surface in liquid-tight sealing contact therewith.

Where seals are used, they must, of course, be capable
10 of generating the required sealing contact with the surface when deformed and not react with the electrolyte. Soft silicone rubbers (shore hardness c.20) can be cast into a suitable shape for use as a seal in the present device but are physically weak and are reactive with some
15 electrolytes. Hard silicone rubbers (shore hardness c.60) do not always make a satisfactory seal. For these reasons, it is preferred to use a seal comprising a soft silicone rubber protected by a harder, thin walled tube. Such a seal may, for example, comprise a tube of a hard elastomer
20 (e.g. 50-60 shore hardness) filled with a soft silicone rubber (e.g. 20 shore hardness). Such a seal may be made by injecting a two-part silicone rubber compound into the tube, acting as a mould, and allowing it to set. The above and other seals can be made in a range of configurations as
25 required: an example is an 'O' ring seal.

If desired, the device may be made of flexible materials so that it can be used in the treatment of
30 significantly non-planar surfaces.

The device of the invention can be used as an in situ electropolishing probe for treating surfaces of Cr or Cr-Ni containing steels known as stainless steels. For example it can be used in the nuclear industry to treat areas of a
35 surface that have become contaminated with radio-active material, i.e. so-called "hot spots", or it can be used to

polish heat exchanger surfaces or surfaces of components used in the food or pharmaceutical industries thereby to make them more resistant to fouling. Also, it can be used to electropolish welds when it may be capable of giving a better surface finish with a smoother microstructure, even at ambient temperature, than known techniques.

Where the metal surface is a stainless steel surface, the electrolyte may suitably be aqueous nitric acid, for example of concentration within the range from 1M to 10M. The aqueous nitric acid electrolyte, if used, may also contain chromium(VI) oxide (CrO_3) which may significantly reduce the magnitude of the current required to electropolish the metal surface. For example, provision of 20% by weight of CrO_3 in 10M HNO_3 is found to reduce the current density for electropolishing stainless steel from 1 Acm^{-2} to 0.5 Acm^{-2} .

For decontaminating surfaces at a high rate in situ, 6M-10M HNO_3 may be a suitable electrolyte. For example, at current densities in the range $0.5 - 2 \text{ Acm}^{-2}$ and temperatures in the range $10 - 35^\circ\text{C}$, a "hot spot" on a contaminated surface may be treated in a few seconds, e.g. 15 seconds, using a device of the invention. A desired decontamination factor may be obtained without dissolving excessive amounts of the surface metal. Also, the surface may be made microsmooth; it therefore picks up less activity subsequently and is easier to clean.

Aqueous nitric acid, optionally containing chromium(VI) oxide, is a suitable electrolyte when the device of the invention is used to electropolish welds. The art describes electropolishing welds using phosphoric acid based electrolytes which, however, have the disadvantage of giving a rough finish due to the different

rates at which the various phases in the weld dissolve. In contrast, the present device can be used in such a way that the phases of the weld dissolve more quickly, hence giving an improved surface finish.

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The device of the invention may be made and used so as to minimise production of bubbles which, if present, in the electrolyte chamber would obscure part of the surface being treated thereby inhibiting electropolishing. The cathode
10 is therefore preferably made of a material such as titanium such that, in operation of the device, production of insoluble gases such as H_2 and NO by the cathode reaction can be suppressed. Where the electrolyte flows through the chamber, its flow rate can therefore be relatively slow,
15 for example about $3 \text{ cm}^3 \text{ s}^{-1}$ for a device having a 25 cm^2 treatment area. When the cathode is a titanium cathode, the device may be operated at high HNO_3 concentrations and high current densities without generating bubbles at the cathode, the nitrate reduction
20 products being soluble gases such as N_2O . Also, the cathode does not lose weight. When production of insoluble gases is suppressed it is possible to operate the device at low electrolyte flow rates when a surface can be treated by a single pass of electrolyte through the device. The
25 rate of flow of electrolyte through the flow channel must, however, be uniform.

The invention will now be particularly described, by way of example only, with reference to the accompanying
30 drawings wherein

Figure 1 is a plan view, from the bottom, of an electrolytic polishing device of the invention showing the working (or polishing)
35 face of the device;

Figure 2 is a section on the line A-A of Figure 1;

Figure 3 is a plan view, from the top, of the device
of Figure 1; and

Figure 4 is a schematic sectional representation of an
electropolishing device of the invention.

Referring to Figures 1 and 2, a housing 1 of
substantially rectangular cross section carries on its
lower surface an inner rectangular recess 2 and an outer
rectangular recess 3. Each recess 2 and 3 carries a
hollow, deformable 'O' ring seal made of a silicone rubber
(neither shown). Mounted within the housing 1 is a
titanium cathode 4 arranged to define an electrolyte flow
channel 5 bounded by the inner recess 2. The cathode 4 is
connectable to a source of electromotive force (not shown)
via a conductor (not shown). The flow channel 5 has an
inlet channel 6 for supplying electrolyte thereto and an
outlet channel 7 for removing electrolyte therefrom. Also
positioned within the housing 1 is a vacuum chamber (not
shown) for applying a vacuum between the seals in the
recesses 2 and 3.

The inlet channel 6 consists of three interconnected
portions: a first cylindrical portion 8, a second
triangular shaped portion 9 for spreading electrolyte flow
as shown in Figure 3, and a third cuboid shaped portion 10
in communication with the flow channel 5.

In operation of the device, it is placed against a
metal surface to be treated and vacuum applied via the
vacuum chamber so that the 'O' ring seals deform in contact
with the surface to make a liquid and gas tight seal
therewith. Electrolyte is passed through the inlet channel

6 and thence into and through the flow channel 5 in the direction shown by the arrow a where it contacts both the cathode 4 and the surface to be treated. The cathode 4 and the surface to be treated, as anode, are connected to the source of electromotive force (not shown) and a current passed thereby to establish and operate an electrolytic cell and hence polish the surface to be treated electrolytically. Used electrolyte, containing anodic oxidation products, is removed from the flow channel 5 via the outlet channel 7.

An example of a device as shown in the drawings had a flow channel 5 of 50 mm width and 50 mm length, i.e. it was capable of treating an area of 50 mm x 50 mm, sufficient to treat most "hot spots". Such a device can be used to treat larger areas by sequential treatment of adjacent squares of the surface; a device having a flow channel 5 of square or rectangular cross section is suitable for treating larger areas sequentially since there is then minimum overlap between adjacent treatment areas. Also, a flow channel 5 of such shape assists uniform flow of electrolyte therethrough.

In practice, the size of the device is limited by the magnitude of the current required and hence the heat produced; however, restriction of size is compensated by the speed of treatment using the device. Examples of sizes of inlet, outlet and flow channels 6, 7 and 5 of the device shown in the drawings are as follows: the diameter of inlet and outlet channels 6 and 7 may be 3 mm or more to reduce electrolyte velocity as the electrolyte approaches the surface to be treated since otherwise the surface would dissolve more quickly where the electrolyte flow changes direction; the height of flow channel 5 may be about 2 mm to enable the electrolyte to sweep any air bubbles away when the device is first filled with electrolyte; and

the height of the outlet channel 7 may be about 30 mm so that the convergence of electrolyte flow towards the outlet channel 7 does not affect the upstream electropolishing effect.

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The device may be designed so that it can be used in both horizontal and vertical orientations.

Referring to Figure 4, the same reference numerals as used in Figures 1-3 are used for similar components. Additionally shown are a metal object being treated 11, where the area 17 on its surface being treated is shown by crosses; hollow, deformable O-ring seals 12 and 13 in each of the recesses 2 and 3 respectively; a tube 14 for connecting to the vacuum pump so that a vacuum can be applied between the seals 12 and 13; the conductor 18 for connecting the cathode 4 to the source of electromotive force (not shown); an electrical connection 15 to the conductor 18; and an electrical connection 16 to the object being treated 11 as anode.

The operation of the device shown in Figure 4 is as described for the device shown in Figures 1-3.

Claims

1. A device for electrolytically treating a metal surface comprising

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a housing connectable to the surface, in liquid-tight sealing contact therewith, to enclose an area of the surface for electrolytic treatment;

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an electrolyte chamber defined within the housing and, when the housing is connected to the surface, bounded in part by said area of the surface;

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a cathode mounted within the housing for contacting electrolyte in the electrolyte chamber thereby to establish an electrolytic cell comprising the cathode, the electrolyte and the surface as anode; and

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means for connecting the cathode and the surface, as anode, to a source of electromotive force.

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2. A device according to claim 1 wherein the housing is connectable to the surface by means of one or more continuous deformable seals.

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3. A device according to claim 2 wherein the seals comprise a tube of a hard elastomer filled with a softer silicone rubber.

4. A device according to claim 2 or claim 3 wherein there is a plurality of concentric deformable seal and means are provided for generating a vacuum therebetween to cause the seals to engage the surface in liquid-tight sealing contact therewith.

5. A device according to any of the preceding claims wherein the electrolyte chamber is bounded in part by the cathode also.
- 5 6. A device according to any of the preceding claims wherein the cathode is made of titanium.
7. A device for electrolytically polishing a metal surface substantially as described herein with reference to
10 any of the accompanying drawings.